THE PENNSYLVANIA STATE COLLEGE

School of Chemistry and Physics

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TECHNICAL REPORT ON CONTRACT

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by

J. G. Aston
Director, Cryogenic Laboratory

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FREE ENERGY OF DISSOCIATION OF AMINE HYDROCHLORIDES AT 25° FROM CELL MEASUREMENTS [1]

(1) Carried out under Contract N6onr-269 T.O. III of the Office of Naval Research.

Sir:

The standard free energy of the reaction

$$RNH_2\ Cl\ (s) = RNH_2\ (g) + HCl\ (g)$$

is a criterion of base strength. It is given by

$$-\Delta F^\circ = R\ T\ \ln P_{RNH_2}\ P_{HCl} \qquad (1)$$

The two pressures can be obtained from the electromotive force of the cell

$$H_2\ (g),\ RNH_2\ (m = x),\ RNH_3\ Cl\ (s),\ Ag\ Cl,\ Ag. \qquad (A)$$

With water as solvent the silver chloride electrode is attacked, but if alcohol be used this difficulty is avoided.

The value of E°_g, for the cell

$$H_{2(g)},\ HCl\ (g),\ Hg\ Cl\ (s)\ Hg. \qquad (B)$$

is $E^\circ = -0.1509$. [2]

(2) J. G. Aston and F. L. Gittler, THIS JOURNAL, 76, 0000 (1954).

From this and the electromotive force of cell A the fugacity of the hydrogen chloride can be calculated.

The partial pressure of the amine can be obtained by passing the exit hydrogen through dilute sulfuric acid then through activated alumina. The total increase in weight together with the amount of amine (as determined by micro-titration) carried over by a measured volume of hydrogen, allow the calculation of the necessary mole fractions to calculate the partial pressure (fugacity) of amine. The methylammonium chloride system has been studied.

In the first measurements in which the alcohol was purified by distilling 95 per cent alcohol over lime followed by final drying with magnesium and iodine and storing under nitrogen, the electromotive force stayed constant for about one hour and then started to fall. Seven values of ΔF° at 298.16°K., with a variation of the amine molality from 0.17 to 0.45, varied between 23,204 and 23,229 cal. The most probable value, calculated using the value of $\Delta H^{\circ}_{298.16}$, [3]

(3) John G. Aston and Charles W. Ziemer, THIS JOURNAL, 68, 1405 (1946).

together with the entropies of methylammonium chloride [3] and methylamine calculated from the spectroscopic data [4] is 22,867 ± 30 cal.

(4) J. G. Aston and Paul J. Doty, J. Chem. Phys., 8, 743 (1940).

The difference is well outside any reasonable error and was at first taken to indicate a possible zero point entropy of R ln 2 in methylammonium chloride. [5]

(5) J. G. Aston, Faraday Society Discussions, No. 10, 73 (1951).

However, as a test of thermodynamic consistency, measurements were made of cell A

at several temperatures between 0° and 40°C., and it was found that the discrepancy was traceable to aldehydes (or other reducable material) in the alcohol. These reduce silver chloride and produce a local excess of chloride ion, thereby making the HCl partial pressure and hence ΔF° appear higher. Finally all alcohol was distilled from ethyl phthalate, sodium and silver nitrate and stored under nitrogen. Excess silver chloride was always placed on the silver side of the cell and the cell were made to come to equilibrium from the high side, as well as the low, by electrolysis. The value of ΔF° at 298.6°K. was finally found to be 22,831 ± 12 cal. The value of $\Delta H^\circ_{298.16}$ obtained from the temperature coefficient agreed with the measured ΔH° [3] within 30 cal. The close agreement with the calorimetric free energy indicates no randomness in methylammonium chloride.

As a matter of interest the corresponding ΔF° at 298.16 for the dissociation of ammonium chloride is 21,860 cal. [6] which is 1000 cal. lower than that for the

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(6) C. C. Stephenson, J. Chem. Phys., 12, 319 (1944).

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methyl substituted deviative. The effect of the methyl group in increasing the basicity of the amine is thus not as great by this criterion as from base strength measurements in aqueous solution which correspond to a 1800 cal difference.

Department of Chemistry
The Pennsylvania State University
State College, Pa.
Doctors Hospital, Cleveland Heights, Ohio
Sylvania Electric Products Inc., Montoursville, Pa.

J. G. Aston
(Miss) Kuo Hao Ha
Frank L. Gittler